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Factors Affecting the Rates of Addition of Free Radicals to Alkenes—Determination of Absolute Rate Coefficients Using the Persistent Aminoxyl Method

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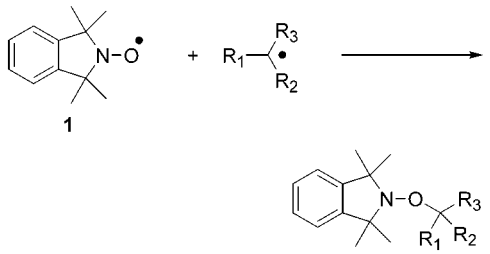
Abstract: The rate of coupling of alkyl radicals with the persistent aminoxyl radical 1,1,3,3-tetramethylisoindolin-*N*-oxyl (**1**) has been used as a kinetic probe to determine absolute rate coefficients for the addition of alkyl radicals to methyl acrylate. The results are discussed in terms of the role of the structure and functionalization of the attacking radical on the rates of addition, particularly as they affect steric, polar, and enthalpic factors. The aminoxyl method is assessed against other methods for determining free radical addition rate coefficients.

Introduction

Persistent aminoxyl radicals have found widespread use in both chemistry and biology as mechanistic and kinetic probes for reactions believed to proceed via carbon-centered free radical intermediates. The utility of species such as 1,1,3,3-tetramethylisoindolin-*N*-oxyl (**1**)[1,2] arises from the fact that they selectively couple with carbon-centered free radicals, generating alkoxylamine adducts.[3]



The coupling reaction is rapid: rate coefficients for coupling k_C with small radicals generally range between 10^8 and 10^9 M^{-1} s^{-1}.[4-7] The availability of rate coefficients for coupling of carbon-centered radicals with **1** and other aminoxyls makes them ideal potential "clocks"[8] for free radical reactions. They have been used successfully in competitive kinetic experiments to determine the rates of unimolecular free radical reactions.[9] For bimolecular free radical reactions the major application of aminoxyl couplings has been the identification of product radicals. In particular, the groups of Rizzardo and Solomon and of Jenkins and Busfield have identified the products arising from the early stages of polymerization[10,11] and the reactions of alkoxyl radicals with various organic substrates.[12,13] Given the obvious success of these groups in isolating and identifying the products of telomerization reactions, it is perhaps surprising that the use of persistent aminoxyl radicals as "clocks" for free radical addition reactions is not more widespread.[14]

In the current work we have determined the rate coefficients and Arrhenius parameters for the addition of a number of free radicals to methyl acrylate using the aminoxyl coupling method and have compared the results obtained with those derived from

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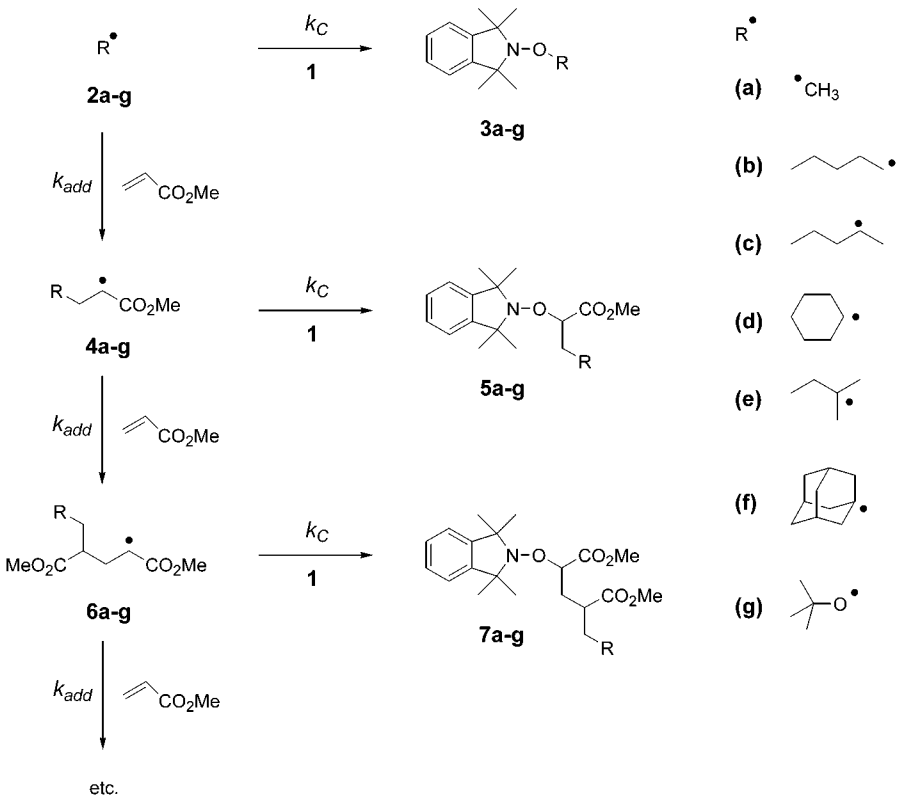
Scheme 1



other methods. The resultant data are discussed in terms of the effect of the structure and functionalization of the attacking radical on the rate of addition to olefins.

Results and Discussion

The Persistent Aminoxyl Method. Scheme 1 shows the reactions that occur under our conditions when alkyl radicals are generated in the presence of methyl acrylate (MA) and the aminoxyl **1**, which was chosen because it is crystalline, is easily purified, and affords adducts that are readily quantified by HPLC/UV. In theory the reaction should produce a mixture of higher oligomers, but in practice the coupling constants k_C are so much larger than the addition constants k_{add} that the formation of products arising from further addition reactions of radical **6** is negligible. Under these circumstances the only stable products formed in detectable concentrations are **3**, **5**, and **7**. The usual treatment of the reactions of Scheme 1 gives the kinetic expressions

$$\frac{d\{[\mathbf{5}]+[\mathbf{7}]\}}{d[\mathbf{3}]} = \frac{k_{add,2}[MA]}{k_C[\mathbf{1}]} \quad (1a)$$

$$\frac{d[\mathbf{7}]}{d[\mathbf{5}]} = \frac{k_{add,4}[MA]}{k_C[\mathbf{1}]} \quad (1b)$$

The difference in the magnitudes of k_C and k_{add} requires the reactions to be conducted with MA in relatively high concentrations and in large excess. Under these circumstances, [MA] remains effectively constant throughout the course of reaction. The observed kinetics are therefore pseudo first order in nature and, thus, allow the relative rate coefficients to be determined analytically from the integrated rate equations (2a) and (2b).

$$\frac{[\mathbf{3}]_t}{\{[\mathbf{5}]+[\mathbf{7}]\}_t} = \frac{[\mathbf{1}]_0 - [\mathbf{1}]_t}{\alpha \ln\left\{\frac{\alpha+[\mathbf{1}]_0}{\alpha+[\mathbf{1}]_t}\right\}} - 1 \quad (2a)$$

$$\alpha = \frac{k_{add,2}[MA]}{k_C}$$

$$\frac{[\mathbf{5}]_t}{[\mathbf{7}]_t} = \frac{[\mathbf{1}]_0 - [\mathbf{1}]_t}{\beta \ln\left\{\frac{\beta+[\mathbf{1}]_0}{\beta+[\mathbf{1}]_t}\right\}} - 1 \quad (2b)$$

$$\beta = \frac{k_{add,4}[MA]}{k_C}$$

The absolute rate coefficients for addition, k_{add}, may be calculated from the relative rate coefficients using published rate coefficients for the coupling of free radicals with **1**, k_C.

The radicals **2b**−**f** were generated in the presence of known amounts of **1** and an internal standard (naphthalene) in monomer between 298 and 355 K. Radicals **2b**−**d** were generated from the corresponding diacyl peroxides and **2d**−**f** from the *tert*-butyl peresters. The precursors for **2d** were chosen on the basis of the temperature employed. Crossover experiments performed at 315 and 333 K demonstrated that identical relative rate coefficients were obtained from both precursors. The use of *tert*-butyl peresters as radical precursors leads to the generation of *tert*-butoxyl radicals, the reactions of which are discussed below.

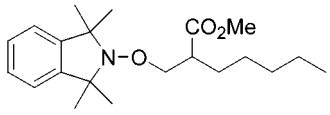
The reactions were carried out in duplicate in neat methyl acrylate at three concentrations of **1** covering an order of magnitude, each at four temperatures within the range 298−355 K. Product analysis was performed by reverse-phase HPLC with detection by UV absorption, and the final concentration

Table 1. Kinetic Data for Addition of Organic Free Radicals to Methyl Acrylate[a]

	rel kinetic data[b]			competing reacn			abs kinetic data for addition		
radical	log (A_{add}/A_C)[c]	$E_{add} - E_C$[c] (kJ mol^{-1})	N[d]		log A_C[e,f]	E_C (kJ mol^{-1})[f]	log A_{add}[e]	E_{add} (kJ mol^{-1})	k_{add}^{298} (M^{-1} s^{-1})
methyl (**2a**)	-1.02 ± 0.52	14.0 ± 3.2	25	**2a** + **1** → **3a**	9.7	3.8	8.7	17.8	3.8×10^5
pentyl (**2b**)	-1.32 ± 0.08	11.1 ± 0.4	30	**2b** + **1** → **3b**	9.7	3.8	8.4	14.9	6.2×10^5
1-methylbutyl (**2c**)	-1.72 ± 0.08	7.2 ± 0.4	35	**2c** + **1** → **3c**	9.7	3.8	8.0	11.0	1.2×10^6
cyclohexyl (**2d**)	-1.39 ± 0.07	6.4 ± 0.4	36	**2d** + **1** → **3d**	9.7	3.8	8.3	10.2	3.3×10^6
1,1-dimethylpropyl (**2e**)	-1.99 ± 0.09	2.6 ± 0.6	28	**2e** + **1** → **3e**	9.7	3.8	7.7	6.4	3.8×10^6
1-adamantyl (**2f**)	-1.00 ± 0.19	-2.6 ± 1.1	16	**2f** + **1** → **3f**	9.7	3.8	8.7	1.2	3.0×10^8
tert-butoxy (**2g**)[g]	-5.13 ± 0.31	-30.0 ± 1.9	25	**2g** + **1** → **3g**	12.7 ± 0.3[g]	47.5 ± 1.1[g]	7.6 ± 0.3	17.5 ± 1.9	3.4×10^4
tert-butoxy (**2g**)[g,h]	-6.0 ± 1.1	-24 ± 7	20	**2g** + **1** → **9c**[i]	12.7 ± 0.3[g]	47.5 ± 1.1[g]	6.7 ± 1.1	23 ± 7	5×10^2
4b[i]	-2.53 ± 0.38	12.6 ± 2.3	10	**4b** + **1** → **5b**	9.7	3.8	7.2	16.4	4.2×10^4
4g[j]	-2.55 ± 0.46	9.1 ± 2.8	25	**4g** + **1** → **5 g**	9.7	3.8	7.1	12.9	6.9×10^4

[a] Tail addition except as otherwise noted. [b] Determined in the temperature range 298−355 K. [c] Errors quoted are 90% confidence intervals for the line of best fit. [d] Number of experiments used to construct the relevant Arrhenius curves. [e] Data shown are *numerical* values only, equivalent to log (A/M s^{-1}). [f] Data from ref 5a unless otherwise specified. As these data were quoted without any experimental uncertainty, the experimental uncertainties of the absolute kinetic data cannot be determined and are not included in this table. [g] Data from ref 18. The competing reaction is unimolecular β-fission. Therefore, the units for A_C and A_{add}/A_C in this case are s^{-1} and M, respectively. [h] Data for head addition to methyl acrylate. [i] 1-(Methoxycarbonyl)heptyl radical. [j] 1-(Methoxycarbonyl)-2-*tert*-butoxyethyl radical.

of **1** was determined relative to naphthalene internal standard. The compounds **3b**−**f** and **5b**−**f** were all isolated and characterized; the compounds **7b**−**f** and **5b(head)**, arising from "head"



5b(head)

addition of the pentyl radical (addition to the substituted end of the monomer), were identified on the basis of HPLC retention times and electrospray mass spectra (ESMS) of the collected fractions. The potential reversibility of the coupling reaction under the reaction conditions, particularly with **2e**, was investigated by obtaining the time-resolved product analysis. Each time point in these experiments yielded the same (within experimental uncertainty) relative rate coefficients, with no apparent increase in α over time. Thus, we conclude that the coupling reaction may be considered effectively irreversible under the conditions used.

Substitution into eq 2a of the experimentally determined concentrations of **1** and addition products yielded the reduced concentration parameter α. Correction of α for the effective concentration of methyl acrylate (equivalent to the value for neat solvent, 11.1 M, with a small dilution factor due to the addition of initiator solution to the reaction mixture) yielded the relative rate coefficients k_{add}/k_C. Arrhenius curves for the relative rate coefficients were constructed for the additions of **2b**−**f** to methyl acrylate. These are shown in Figure 1. A summary of relative Arrhenius parameters is shown in Table 1.

At low concentrations of **1**, the alkoxylamine product **7b** arising from secondary addition reactions could be reliably identified and quantified in product mixtures. This allowed relative rate coefficients and Arrhenius parameters for the addition of **4b** to methyl acrylate to be estimated (Table 1). These parameters are subject to a relatively high degree of experimental uncertainty, because only small amounts of the coupling product **7b** are observable at low concentrations of **1**. At higher concentrations of **1**, the observed levels of **7b** fall below the limit of quantification of the method.

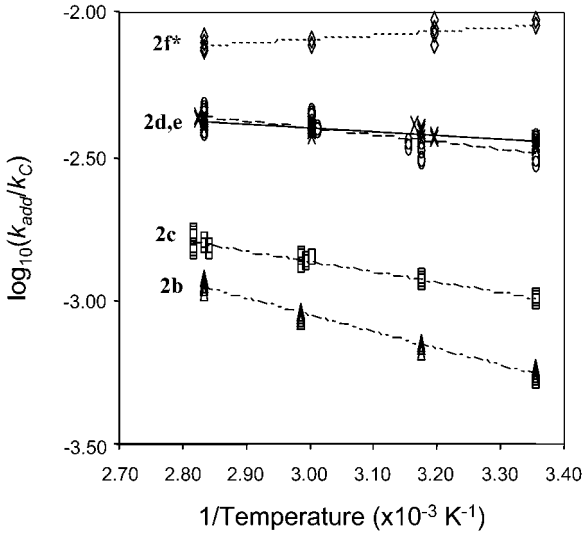
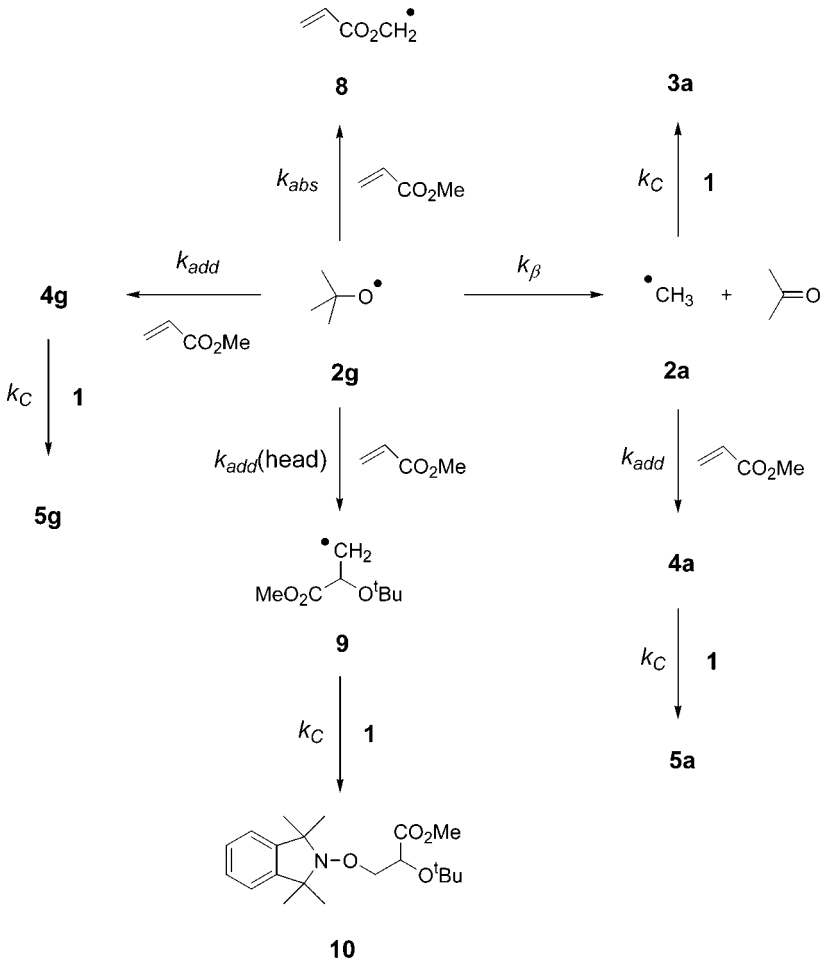


Figure 1. Relative Arrhenius plots of k_{add}/k_C for reactions of radicals **2b** (triangles), **2c** (squares), **2d** (circles), **2e** (crosses), and **2f** (diamonds) by addition to methyl acrylate and by aminoxyl coupling. log(k_{add}/k_C) data for **2f** are shifted by −2.5.

The *tert*-Butoxyl Radical. Thermal decomposition of *tert*-butyl peresters in the experiments described above for **2d**−**f** generates the highly reactive *tert*-butoxyl radical **2g**. The various reactions of **2g** relevant to the present work are shown in Scheme 2.

β-Fission of **2g** generates $CH_3^\bullet$ (**2a**), which adds to methyl acrylate to afford the radical **4a**. Radical **2g** also reacts directly with methyl acrylate by hydrogen atom abstraction to afford **8** or by addition to afford **4g** and **9**, which couple with **1** to afford **5g** and **10**, respectively. Under the conditions of the present work **4g** also undertakes secondary addition to methyl acrylate, thus generating radical **6g**, which couples with **1** to afford **7g**. Since the reactions of **2g** with methyl acrylate in the presence of **1** have been previously studied,[10a,b] the final products (**3a**, **5a**, **5g**, **7g**, and **10**) could be identified simply on the basis of chromatographic retention and ESMS. The compound **5g** was isolated and characterized as a confirmation of the retention order. The resolution of peaks corresponding to products arising from **8** was insufficient to provide reliable quantification of these products, and thus these addition reactions could not be studied.

Scheme 2



Because radical **2g** does not react directly with **1**, the usual aminoxyl coupling cannot be used to determine the relative rates of reactions of **2g** with methyl acrylate. Fortunately, the rate coefficients and Arrhenius parameters for the β-fission reaction **2g** → **2a** are known,[15] and this reaction therefore serves as a clock for reactions of **2g**. Kinetic analysis yields expressions similar to eq 1 for determination of the k_{add} for "head" and "tail" addition of Bu^{t}O$^\bullet$ to methyl acrylate relative to the corresponding constant (k_β) for its β-fission. The relative rate coefficients and Arrhenius parameters for reactions leading to the formation of **4a**, **4g**, **6g**, and **9** are summarized in Table 1.

Absolute Rate Data for the Addition of Free Radicals to Methyl Acrylate. Absolute values of the rate coefficients and Arrhenius parameters for the various reactions discussed above were determined by comparison of the relative values with the corresponding absolute values for the competing reaction. The choice of appropriate kinetic data for coupling of carbon-centered radicals with **1** was problematic, due to recent work[7] which has demonstrated that many reactions of this type do not exhibit linear Arrhenius behavior. However, earlier work[4,5a] has indicated that that coupling of simple alkyl radicals to **1** gives a good linear correlation of k_C with $1/T$ over the temperature range studied, and this is supported by the linear behavior of the relative data shown in Figure 1. Unfortunately, the limited amount of data available from direct methods (LFP) is restricted to single temperatures.[4,5] They indicate that aminoxyl coupling is probably under entropic control and that the order of reactivity for alkyl radicals is 1° > 2° > 3° but covers a narrow range from $k_C = 1.3 \times 10^9$ M^{-1} s^{-1} for pentyl to 9.1×10^8 M^{-1} s^{-1} for *tert*-butyl at 298 K. Because of the lack of more reliable data, we decided to use the general expression obtained from indirect methods and recommended by Beckwith et al.[5a] for the rate coefficient for coupling of carbon-centered free radicals with **1** (k_C; R in J mol^{-1} K^{-1}):

$$\log_{10}(k_C\ (\mathrm{M\ s})) = 9.7 - (3800/2.303RT) \qquad (3)$$

It should be noted that although our measurements are subject to a small degree of uncertainty, the use of a single expression for k_C, for which no experimental uncertainties were cited, does provide a significant (but unknown) degree of uncertainty in our measurements. For this reason, we have not included uncertainties for values of log A_{add} and E_{add} in Table 1. Given the observations of previous workers, we expect that absolute rate constants for addition to methyl acrylate obtained from eq 3 will tend to be low for methyl radical and high for tertiary radicals, with variations mainly reflected in a narrow range of values for log A_{add}. E_{add} would also be expected to vary only within a relatively narrow range of values. Thus, the discrepancies arising from this approach should be small and should not affect the general trends revealed by our experiments.

For the "head" and "tail" additions of Bu^{t}O$^\bullet$ to methyl acrylate the kinetic data for the β-fission reaction were used as reference (R in J mol^{-1} K^{-1}):[15]

(15) Weber, M.; Fischer, H. *J. Am. Chem. Soc.* **1999**, *121*, 7381−7388.

$$\log_{10}(k_\beta\,(\mathrm{s})) = (12.7 \pm 0.3) - (47.5 \pm 1.1) \times 10^3/2.303RT),\ R \text{ in Jmol}^{-1}\,\mathrm{K}^{-1} \quad (4)$$

The derived rate coefficient data for addition of carbon-centered free radicals to methyl acrylate are summarized in Table 1.

With the data from Table 1 in hand, the results obtained by the persistent aminoxyl method can be compared with data obtained from direct kinetic EPR (KEPR) measurements[16−18] and, to a lesser extent, from pulsed laser polymerization (PLP) studies.[19] There is only a relatively limited data set available for comparison, and the useful data is summarized in Table 2.

Generally there is good agreement between the data obtained by the KEPR and aminoxyl methods for methyl radical[16] (entries 1 and 2) and primary (entries 3−4) and secondary radicals (entries 5 and 6).

Comparisons of the values for tertiary radicals obtained from KEPR[18] and persistent aminoxyl-based methods (entries 7 and 8) exhibit a greater disparity. This is presumably due to the fact that a single expression for k_C is unlikely to hold for all carbon-centered radicals. In addition, the quoted value of E_{add} is that calculated by Fischer et al.[18] from an average value of A_{add} observed for a number of other olefins and may, therefore, be subject to some uncertainty.

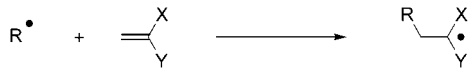
Factors Affecting the Rates of Addition of Free Radicals to Olefins. The factors affecting the rate and selectivity of free radical addition to olefins in solution have received significant attention over time and have been extensively reviewed by Tedder, Walton,[20] and Giese.[21] Most recently, Fischer and Radom[22] have extended and improved the treatment of radical additions by earlier qualitative models and have developed a quantitative, parametrized model for radical additions to alkenes. All workers have agreed that no single interaction adequately describes the variation in rate and selectivity (chemo-, regio-, and stereoselectivity) observed in these systems: i.e., these reactions are governed by a "complex interplay of polar, steric and bond strength terms".[21a]

Fischer et al.[16−18,23−25] have demonstrated in a number of studies that, for the addition of a radical species R$^\bullet$ with a series of functionalized olefins, the rate coefficients could be modeled using a single value of log A_{add} (dependent on the structure of R$^\bullet$). The activation energies observed exhibited good correlation with the energy differences between SOMO and LUMO of the radical−olefin pair (the ionization potential of the radical minus the electron affinity of the olefin), consistent with a charge-transfer FMO approach to polar effects.

Table 2. Comparison of Kinetic Data Obtained by the Persistent Aminoxyl and Other Methods for the Addition of Alkyl Radicals to Methyl Acrylate

entry	radical	method	log (A_{add} (M s))	E_{add} (kJ mol^{-1})	k_{add}^{298} (M^{-1}s^{-1})
1	methyl (**2a**)	aminoxyl	8.7	17.8	3.8×10^5
2	methyl (**2a**)[a]	KEPR	8.5[b]	16.9[c]	3.4×10^5
3	1-pentyl (**2b**)	aminoxyl	8.4	14.9	6.2×10^5
4	2-(*tert*-butoxycarbonyl)-methyl[a]	KEPR[1]	8.4[b]	15.5[c]	4.9×10^5
5	1-(methoxycarbonyl)-heptyl (**4b**)	aminoxyl	7.2	16.4	2.1×10^4
6	butyl acrylate polymer[d]	PLP	7.2	17.3	1.5×10^4
7	1,1-dimethylpropyl (**2e**)	aminoxyl	7.7	6.4	3.8×10^6
8	*tert*-butyl	KEPR	7.3[a]	7.2[c]	1.1×10^6

[a] Data from ref 16. [b] Values used are an average value for log A determined for the reaction of the target radical with several olefins.[16−18,22] [c] The activation energies are calculated from the experimental rate coefficients and the average Arrhenius preexponentials.[16−18,22] [d] Kinetic data obtained from pulsed laser polymerization.[19]



More recently, Fischer and Radom[22] have demonstrated that the activation energy for these reactions may be modeled by an Evans−Polyani−Semenov approach, which provides an upper limit for E_{add} based on the enthalpy of reaction. The Evans−Polyani−Semenov limiting value for E_{add} is then corrected by polar effects, parametrized in terms of multiplicative polar factors (MPFs). It is clear, therefore, that bond strength, stabilization, and polar effects are not readily separable in these reactions.

In this study, we have attempted to determine the effect of changing the structure and functionalization of R$^\bullet$ on the rate of addition to a single olefin (methyl acrylate). Fischer's results indicate that polar effects should be important, and a number of previous workers have demonstrated the significance of steric effects on these reactions.[20,21] We have, therefore, attempted to rationalize our observed data by reference to such effects.

Steric Effects. It is widely accepted that for the Arrhenius model the preexponential factor reflects the change of motional degrees of freedom accompanying the formation of the transition structure**.** For the addition of a series of neutral radicals to a given olefin in a single solvent the effect should become increasingly unfavorable with increasing steric bulk of the radical. Hence, in the present work the value of log A_{add} is expected to decrease down the series primary > secondary > tertiary. This is clearly shown in Table 1 for the reactions of **2a**−**d**. For rigid or otherwise constrained radicals the effect is expected to be less than that for more flexible analogues; thus, log A_{add} for cyclohexyl is greater than that for the secondary radical **2d**, while log A_{add} for 1-adamantyl is the same as that for methyl.

For a more quantitative approach, we expect that the observed values of A_{add} in Table 1 should show a correlation with an appropriate steric factor. Two possible steric parameters have been considered: the traditional Taft steric parameter, E_S,[26] and the Ω_S scale of Sakakibara et al. (Table 3).[27]

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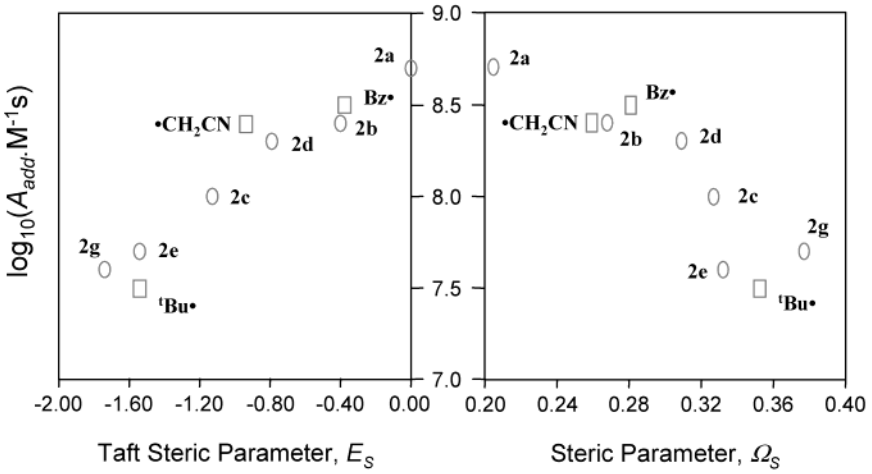

Figure 2. Correlation of observed Arrhenius preexponentials for addition of free radicals to methyl acrylate with the Taft steric parameter E_S, and the Ω_S parameter of Sakakibara et al. Data shown are from this work (○) and from the literature (□, refs 18 and 23a). The values of E_S and Ω_S for **2g** were assumed to be equivalent to those of a neopentyl group.

Table 3. Values of log A_{add}, E_S, and Ω_S for Selected Organic Free Radicals

radical	log A_{add}[a,b]	E_S[c]	Ω_S[d]
methyl (**2a**)	8.7	0	0.205
1-pentyl (**2b**)	8.4	−0.40	0.269
1-methylbutyl (**2c**)	8.0	−1.13	0.329
cyclohexyl (**2d**)	8.3	−0.79	0.309
1,1-dimethylpropyl (**2e**)	7.7	−1.54	0.377
tert-butyl	7.3	−1.54	0.352
tert-butoxy (**2g**)	7.6	−1.74[e]	0.332[e]
benzyl	8.5[f]	−0.38	0.281
cyanomethyl	8.4[g]	−0.94	0.259

[a] From present work unless otherwise specified. [b] Footnote *c* in Table 1. [c] Reference 26. [d] Reference 27a. [e] Approximated by the value for the neopentyl group. [f] Reference 23a. [g] Reference 18.

The derivation of these parameters is distinct: The Taft parameter E_S is defined in terms of strain energy (an enthalpic property) but should still provide some indication of the extent to which steric hindrance will affect the loss of translational and rotational degrees of freedom in the transition structure. In contrast, Ω_S is obtained from molecular mechanics optimized structures and represents the restriction of approach of the reacting moieties due to the steric size of substituents (calculated by combined van der Waals radii of attached groups). The correlation of A_{add} values obtained in this work, and those values for benzyl and cyanomethyl radicals obtained by Fischer et al., with E_S and Ω_S are shown in Figure 2.

The correlations obtained are quite good, when one considers that (a) the steric factor for **2g** was approximated as being equivalent to that of a neopentyl group and (b) both steric scales are intended to model the effects of substituents attached to carbons α to the reactive site, rather than substituents directly attached to the active site. It should be noted that recently Ω_S values were calculated for alkyl radicals[27b] and that the small number of species considered above for which $\Omega_S^{\bullet}$ values have been calculated show a qualitatively similar correlation. Although it is unlikely that such a close correlation will hold universally for all radical−olefin pairs, particularly those for which there are large polar effects, further examination of the use of steric parameters as predictors of log A_{add} in radical reactions appears to be warranted.

Steric factors are also expected to affect the magnitude of E_{add}, since for bulky radicals the formation of the transition structure should involve an increase in strain energy. The data in Table 1 which show that E_{add} *decreases* with increasing bulk down the series **2a**−**e** indicate that this is not the case for this type of reaction. Clearly other factors come into play (see below). However, the value of E_{add} for adamantyl radical, although suspiciously low, may reflect the fact that the SOMO of this radical has a greater degree of s character than acyclic alkyl radicals. Consequently, the reaction of **2f** with methyl acrylate should have a particularly early transition state and will be especially insensitive to steric effects, leading also to a higher than expected value of log A_{add}.[28]

The selectivity of addition also reflects steric phenomena, consistent with the qualitative observations of Tedder, Walton, and Giese.[20,21] Addition adjacent to the functional group (so-called "head" addition) is believed to be disfavored on steric grounds, and in this study only the relatively sterically undemanding 1-pentyl radical was observed to add to methyl acrylate in the "head" mode, although in insufficient yield to allow the rate to be measured. The *tert*-butoxyl radical was also observed to add in this mode, but this is due in large part to polarity effects (see discussion below).

Bond Strength and Stabilization Effects. The recent review of Fischer and Radom[22] has demonstrated that the activation energies for the addition of a free radical to a range of olefins may be well described by consideration of the components of a state correlation model. We therefore seek to determine whether the activation energies for addition of a range of free radicals to a single olefin show similar correlations. As a first approximation, we consider a Evans−Polyani−Semenov approach, where E_{add} is plotted against ΔH_r for the addition reaction. ΔH_r is calculated for the gas-phase reaction using a group additivity approach to ΔH_r analogous to that of Fischer and Radom. Thus ΔH_r(R,MA) is estimated by[22]

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Table 4. Bond Dissociation Enthalpies (BDE) and Ionization Potentials (IP(R•)) for Selected Organic Free Radicals and Their Heats of Reaction (ΔH_r(R,MA)) and Activation Energies (E_{add}) for Addition to Methyl Acrylate

radical	E_{add}[a] (kJ/mol)	BDE[b] (kJ/mol)	$\Delta H°_f$(RH)[b] (kJ/mol)	$\Delta H°_f$(RCH_2CH_3) (kJ/mol)[b]	ΔH_r(R,MA) (kJ/mol)	IP(R•)[c] (eV)
methyl (**2a**)	17.8	439	-74.9 ± 0.5	-104.7 ± 0.5	−117	9.84
pentyl (**2b**)	14.9	420	-146.8 ± 0.6	-187.8 ± 0.8	−109	7.94
1-methylbutyl (**2c**)	11.0	411	-146.8 ± 0.6	-192.3 ± 1.3	−105	7.41
cyclohexyl (**2d**)	10.2	400	-123.1 ± 0.8	-171.8 ± 1.5	−97	7.66
1,1-dimethylpropyl (**2e**)	6.4	404	-153.7 ± 0.6	−201.2	−100	6.65
1-adamantyl (**2f**)	1.2	403[d]	-134.4 ± 2.3	-190.4 ± 3.0[e]	−108	6.21
tert-butoxy (**2g**)	17.5	440	-312.6 ± 0.9	-350.8 ± 2.6	−89	
1-(methoxycarbonyl)heptyl (**4b**)	16.4	400[f]	−438[g]	−488[h]	−98	7.70[i]
benzyl	26.6[j]	370	50.0 ± 0.6	-7.8 ± 0.8	−61	7.20
cyanomethyl	17.7[k]	389	74.1 ± 0.4	-5.8 ± 1.0	−48	10.87

[a] Data from the present study unless otherwise specified. [b] Data from ref 30 otherwise specified. [c] All data are calculated for gas phase and were obtained from ref 29 unless otherwise indicated. [d] Reference 31. [e] Reference 32. [f] Reference 33. [g] Modeled by methyl propanoate, heat of formation calculated at HF/6-31G*.[34] [h] Modeled by methyl isovalerate, heat of formation calculated at HF/6-31G*.[34] [i] Reference 25. [j] Reference 23a. [k] Reference 18.

$$\Delta H_r(\mathrm{R,MA}) = \Delta H_f(\mathrm{RCH_2CH_3}) - \Delta H_f(\mathrm{CH_3CH_2CH_3}) - \Delta H_f(\mathrm{RH}) + \Delta H_f(\mathrm{CH_4}) - \mathrm{BDE(RH)} + \mathrm{BDE(CH_4)} \quad (5)$$

where BDE is the C−H bond dissociation enthalpy for each species. The value of ΔH_r for methyl radical addition to methyl acrylate has been determined as −117 kJ mol^{-1}, and the remaining thermochemical data are available from NIST databases[29] or the literature.[30−34] The relevant data are shown in Table 4.

Comparison of the data for E_{add} and ΔH_r(R,MA) demonstrates that no simple correlation exists between the activation energy and the enthalpy of reaction and that the simple Evans−Polyani−Semenov model does not apply. Fischer and Radom[26] have found that, for many addition reactions, an accurate model for the rate coefficients cannot be constructed without considering polar effects.

Polar Effects. Initially, the charge-transfer interactions for such a system were described by a frontier molecular orbital (FMO) model, as developed by Fukui[35] and successfully applied to similar systems by Giese[21a] and Fischer et al.[16−18,23−25] This model indicates that the delocalization stabilization of a nucleophilic radical−olefin system as it evolves from reactant to transition state will depend on the energies of the olefin LUMO and the radical SOMO, determined experimentally as the electron affinity (E_{ea}) and ionization potential (IP) of the olefin and radical, respectively.

The state correlation model uses the same parameters to model the energies of the charge transfer states—the lower the energy of the charge transfer states, the greater the configuration mixing and stabilization of the ground state, and the favorable interactions of the charge transfer states are those characterized by large values of the parameters IP(MA) − E_{ea}(R•) or IP(R•) − E_{ea}(MA).

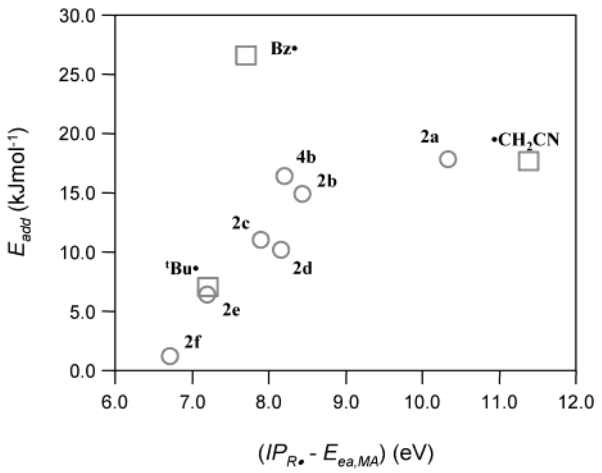

Figure 3. Correlation of the observed activation energies for addition of free radicals to methyl acrylate with the charge transfer state parameter IP(R•) − E_{ea}(MA), with E_{ea}(MA) = −0.5 eV:[26] (○) this work; (□) Fischer et al. Values for cyanomethyl radical and **4b** are gas-phase ionization potentials calculated by ab initio MO methods. No experimental error bars have been included for E_{add} (see footnote *f* in Table 1).

Because methyl acrylate is an olefin with a strongly electron withdrawing group, the "tail" end of the olefin may be considered relatively electron poor. Stabilizing interactions will be observed for nucleophilic radicals attacking the tail position and electrophilic radicals attacking the head position. We thus expect a strong correlation of E_{add} with IP(R•) − E_{ea}(MA) for nucleophilic radicals, and such behavior is observed in Figure 3 for simple alkyl radicals. On the basis of the Fukui FMO formalism, we would expect to see an even better correlation with the inverse of the above charge transfer function, and this is indeed observed for nucleophilic radicals. For electrophilic radicals, the correlation is less marked as expected and is due to the fact that the charge transfer states for electrophile−electrophile systems are of higher energy. The same phenomenon may be alternatively described as a change in the exchange integral β in the older Fukui FMO formalism.[35]

The data for addition of the benzyl radical to methyl acrylate measured by Fischer et al.[23a] indicates the benzyl radical represents a special case with regard to polar effects, presumably due to its high degree of stabilization, as indicated by Fischer and Radom.[22]

The correlation observed for the effect of philicity on the rate of addition is almost certainly characteristic for methyl acrylate. Fischer et al.[17,18,23−25] have demonstrated that changes

(29) Thermochemical data may be found at the National Institute of Standards and Technology (NIST) Chemistry WebBook: http//webbook.nist.gov.
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in correlation between the electron affinities of olefins and the observed activation energies for addition of a specific radical (in particular, the slope of the line of best fit for these parameters) reflect the philicity of that radical. It is logical that the converse should hold true. In addition, we have not considered the steric component of E_{add} in this analysis. It is apparent, however, that the component will not be large for these systems and that E_{add} is dominated largely by polar effects in the system under investigation. This is to be expected, as there is significant separation (approximately 2.15 Å from MO calculations)[21c,36] of attacking radical and the olefin in the transition state. Of course, for truly bulky radicals such as triphenylmethyl, a significant steric component in the observed E_{add} is expected.

The selectivity of addition is also affected by polar factors. For example, the electrophilic *tert*-butoxyl radical exhibits significant "head" addition, despite the relatively unfavorable steric interactions. In addition, the head addition of pentyl radical was observed (but could not be quantified). Unfortunately, neither the thermochemical (ground state) or polar (charge transfer states) correlations are capable of addressing the question of regioselectivity in their current forms. It is possible, however, that the regioselectivity of additions could be predicted once the thermochemistry (ΔH_R) of head addition of methyl radical to methyl acrylate could be determined.

Conclusions

We have conducted a series of experiments designed to test the use of radical coupling reactions of the aminoxyl **1** as kinetic yardsticks for determining the rates of addition of free alkyl radicals to olefins. The results demonstrate that when coupling rates are calibrated by reference to the best available data, the method is capable of affording rate coefficients and Arrhenius parameters comparable with reliable literature values.

Although the set of data obtained in this work cannot be readily tested against the kinetic model recently proposed by Fischer and Radom,[22] it appears that the results conform to long-held views of the influence of polar, steric, and enthalpic effects on the rates of radical addition reactions. Thus, for the addition of nonbenzylic radicals to methyl acrylate, the activation energy exhibits a strong correlation with parameters describing charge transfer states (polar interactions), reflecting the nucleophilicity of the attacking species. The observed values of log A_{add} for the addition reaction depend on radical structural features expected to affect the change in motional degrees of freedom upon formation of the transition structure. Interestingly, a good correlation was observed with appropriate values of the Taft steric parameter E_S and, to a lesser extent, with the Sakakibara Ω_S parameter. Although these parameters have previously been considered to reflect mainly enthalpic factors (e.g. strain energy), it now appears that they may be useful measures of entropic effects. Their potential as indicators of relative values of log A for radical reactions in general and addition reactions in particular deserves further exploration. Interestingly, kinetic data available in the literature from work involving different experimental approaches conform well to the same correlations of log A_{add} and E_{add} as those that apply to our own results. This provides further illustration of the reliability of our method.

In summary, the persistent aminoxyl method involving **1** provides reliable kinetic data for the addition of a variety of simple and substituted alkyl radicals to methyl acrylate. Furthermore, the results suggest that the method could be particularly useful when more direct experimental methods are not readily available and might be applicable to kinetic studies of a much wider range of radical reactions, thus affording data for testing the utility of modern theoretical approaches.

Experimental Section

Materials and Instrumentation. All solvents and synthetic precursors, unless otherwise described, were obtained from commercial sources and were used as received without further purification. Water used in RPHPLC analysis was deionized by a Milli-Q filtration apparatus. RPHPLC analysis was performed using an Alltech Alltima C18 5 μm column (250 mm × 4.6 mm i.d.) with Waters 510 HPLC pumps and a Waters 486 UV−visible detector set at 270 nm.

^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were obtained with a Varian Gemini 300 FT instrument. FTIR spectra were obtained using a Perkin-Elmer 1600 laser FTIR from solutions of the compounds in $CDCl_3$, unless otherwise specified. UV−visible spectra were collected digitally with a Shimadzu UV-2101 PC spectrometer. Mass spectra were obtained with a Fisons VG Autospec mass spectrometer. Electrospray MS were obtained using a Fisons VG Quattro II mass spectrometer.

1 was synthesized as previously described[2] and recrystallized twice from hexane prior to use. Diacyl peroxides were obtained by standard methods,[37] and *tert*-butyl peresters were prepared by one of two methods.

Method A. A solution of pyridine (1.7 mol equiv) and *tert*-butyl hydroperoxide (1.2 mol equiv) in pentane (10 mL) was cooled to 4 °C, whereupon a solution of the appropriate acyl chloride (1.0 mol equiv) in pentane (10 mL) was added dropwise with vigorous stirring. The reaction mixture was warmed to room temperature and stirred for a further 2 h. The pentane solution was washed with water, 2 M H_2SO_4 solution, and saturated $NaHCO_3$ solution (1 × 10 mL each) and dried ($MgSO_4$) and the solvent removed under reduced pressure.

Method B. Sodium *tert*-butylperoxide (2.0 mol equiv) was suspended in dry ether (40 mL), and the resultant mixture cooled to 0 °C, whereupon a solution of the appropriate acyl chloride (1.0 mol equiv) in dry ether (10 mL) was added dropwise with vigorous stirring. The solution was warmed to room temperature and stirred for a further 5 h. Water (10 mL) was added to the reaction mixture, which was stirred overnight at 4 °C. The workup is identical to that of method A.[38]

Aminoxyl Experiments. The following procedure for generation of **2b** in the presence of methyl acrylate and **1** is typical: a solution of bis(hexanoyl)peroxide in *n*-heptane (10−50 μL) was added to a solution of known concentrations of **1** and naphthalene (internal standard) in methyl acrylate (5 mL). The combined solution was degassed using a freeze−pump−thaw cycle (five cycles), sealed, and immersed in a constant temperature oil bath for the requisite period of time, which varied from 2 h at 353 K to 20 days at 298 K. The reaction mixture was then subjected to RPHPLC analysis. $[\mathbf{1}]_0$ and $[\mathbf{1}]_{final}$ were determined relative to naphthalene, and [MA] was assumed to be equivalent to the value of neat solvent, corrected by a dilution factor due to the addition of initiator solution (assuming that the final volume of solution is equivalent to the sum of the volumes of the component solutions). Finally, with the ratios of product alkoxylamines (**3a**, **5a**, and **7a**) in hand, the roots of eqs 2a and 2b (α and β, as and where applicable) were determined by Newton−Raphson techniques to yield values for the effective relative rate coefficients. Where *tert*-butyl peresters were used, the product distributions due to **2g** were fitted independently of the product distributions due to **2d**−**f** to yield relative

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rate coefficients. However, $[\mathbf{1}]_0$, $[\mathbf{1}]_{fina,l}$ and [MA] were determined exactly as described above for *both* initiator fragments.

Authentic samples of alkoxylamine adducts were obtained from semipreparative HPLC of combined reaction mixtures.

2-Pentoxy-1,1,3,3-tetramethylisoindoline (3b). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23 (m, 2H); 7.10 (m, 2H); 3.92 (t, J = 6.6 Hz, 2H); 1.63 (br. tt, J = 6.6, 7.1 Hz, 2H); 1.43 (br. s, 18H); 0.94 (t, J = 6.9 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.2, 127.0, 121.4, 77.4, 67.0, 28.9, 28.6, 22.6, 14.0 ppm. FTIR ($CDCl_3$): ν 2963, 2933, 2872 cm^{-1}. EIMS: *m*/*z* 261 (18), 246 (100), 190 (22), 176 (82), 160 (23), 158 (27), 145 (28). HRMS: $C_{17}H_{27}NO$ requires *m*/*z* 261.2093, found *m*/*z* 261.2091.

2-(1-Methylbutoxy)-1,1,3,3-tetramethylisoindoline (3c). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.24 (m, 2H); 7.11 (m, 2H); 3.93 (tq, J = 6, 6 Hz, 1H); 1.72 (m, 1H); 1.53, 1.50, 1.38, 1.32 (4 × br s, 12H, overlying 1.50−1.40 (m, 3H)); 1.25 (d, J = 6.1 Hz, 3H); 0.97 (t, J = 7.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.4, 145.4, 126.9, 121.4, 78.6, 67.5, 67.1, 38.3, 30.5, 30.0, 25.2, 25.2, 19.8, 18.9, 14.3 ppm. FTIR ($CDCl_3$): ν 2966, 2932, 2873 cm^{-1}. EIMS: *m*/*z* 261 (17), 246 (8), 191 (37), 176 (100), 160 (24), 158 (26), 145 (23). HRMS: $C_{17}H_{27}NO$ requires *m*/*z* 261.2093, found *m*/*z* 261.2086.

2-(Cyclohexyloxy)-1,1,3,3-tetramethylisoindoline (3d). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.22 (m, 2H); 7.10 (m, 2H); 3.70 (m, 1H); 2.10 (m, 2H); 1.77 (m, 2H); 1.50 (s, 6H); 1.35 (s, 6H), overlying 1.24−1.44 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.3, 127.0, 121.5, 81.6, 67.2, 32.5, 30.3, 25.9, 25.2, 24.4 ppm. FTIR ($CDCl_3$): ν 2975, 2934, 2857 cm^{-1}. EIMS: *m*/*z* 273 (22), 258 (9), 191 (56), 177 (61), 176 (100), 160 (26), 158 (39), 145(40), 144 (37). HRMS: $C_{18}H_{27}NO$ requires *m*/*z* 273.2093, found *m*/*z* 273.2091.

2-(1,1-Dimethylpropoxy)-1,1,3,3-tetramethylisoindoline (3e). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23 (m, 2H); 7.09 (m, 2H); 1.62 (q, J = 7.6 Hz, 2H); 1.48 (s, 6H); 1.32 (s, 6H); 1.25 (s, 6H); 0.96 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 145.9, 127.1, 121.8, 78.8, 68.2, 35.5, 30.6, 26.2, 25.7, 9.2 ppm. FTIR ($CDCl_3$): ν 2975, 2930 cm^{-1}. EIMS: *m*/*z* 261 (13), 245 (11), 190 (43), 175 (100), 157 (19), 145 (18). HRMS: $C_{17}H_{27}NO$ requires *m*/*z* 261.2093, found *m*/*z* 261.2089.

2-(1-Adamantyloxy)-1,1,3,3-tetramethylisoindoline (3f). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23 (m, 2H); 7.07 (m, 2H); 2.18 (br s, 3H); 1.87 (br d, J = 3.2 Hz, 6H); 1.65 (br d, J = 2.8 Hz, 6H); 1.49 (s, 6H); 1.34 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.6, 126.9, 121.6, 75.2, 67.8, 46.3, 43.2, 36.4, 31.0, 30.6, 25.7 ppm. FTIR ($CDCl_3$): ν 2976, 2914, 2853 cm^{-1}. EIMS: *m*/*z* 325 (2), 176 (10), 135 (100). HRMS: $C_{22}H_{31}NO$ requires *m*/*z* 325.2406, found *m*/*z* 325.2406.

2-[1-(Methoxycarbonyl)heptanoxy]-1,1,3,3-tetramethylisoindoline (5b). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.22 (m, 2H); 7.09 (m, 2H); 4.43 (t, J = 6.6 Hz, 1H); 3.76 (s, 3H); 1.95−1.65 (m., 2H); 1.56,1.43,1.41 (3 × s, 12H) overlying 1.20−1.55 (m, 8H)); 0.91 (t, J = 6.7 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 174.0, 144.9, 144.6, 127.2, 127.1, 121.5, 121.2, 85.0, 68.0, 67.6, 51.3, 32.2, 31.5, 29.5, 25.4, 25.0, 29.1, 25.2, 22.5, 14.0 ppm. FTIR ($CDCl_3$): ν 2956, 2928, 2858, 1741 cm^{-1}. EIMS: *m*/*z* 347 (12), 332 (58), 190 (100), 176 (38), 160 (28), 158 (24), 145 (23). HRMS: $C_{17}H_{27}NO$ requires *m*/*z* 347.2460, found *m*/*z* 347.2464.

2-[1-(Methoxycarbonyl)-3-methylhexanoxy]-1,1,3,3-tetramethylisoindoline (5c). The obtained product was a mixture of diastereomers, not readily separable under the chromatographic conditions used for kinetic analysis of the reaction mixtures. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.22 (m, 2H); 7.09 (m, 2H); 4.43 (2 × overlying dd, J = 7 Hz, 1H); 3.74 (2 × s, 3H); 1.95−1.82 (m, 1H); 1.80−1.60 (m, 2H); 1.55, 1.38 (2 × s, 3H + 9H) overlying 1.20−1.55 (m, 4H); 0.97, 0.96 (2 × d, J = 6.7, 6.4 Hz, 3H); 0.89 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 174.4, 174.2, 144.9, 144.6, 127.2, 127.2, 127.1, 127.1, 121.5, 121.3, 83.6, 83.2, 68.2, 68.1, 67.6, 67.5, 51.3, 39.6, 39.4, 39.4, 39.2, 30.4, 29.5, 25.5, 25.0, 28.9, 28.9, 19.8, 19.7, 14.2, 14.1 ppm. FTIR ($CDCl_3$): ν 2958, 2930, 2872, 1741 cm^{-1}. EIMS: *m*/*z* 347 (16), 332 (39), 190 (100), 176 (34), 160 (29), 158 (23), 145 (23). HRMS: $C_{17}H_{27}NO$ requires *m*/*z* 347.2462, found *m*/*z* 347.2460.

2-[2-Cyclohexyl-1-(methoxycarbonyl)ethoxy]-1,1,3,3-tetramethylisoindoline (5d). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24 (m, 2H); 7.08 (m, 2H); 4.62 (t, J = 6.9 Hz, 1H); 3.75 (s, 3H); 1.59 (s, 3H), overlying 1.57−1.83 (m, 7H); 1.44, 1.42, 1.41 (3s, 9H); 1.25 (m, 4H); 0.94 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 174.2, 144.8, 144.5, 127.2, 127.1, 121.5, 121.2, 82.9, 68.3, 67.7, 51.3, 39.8, 33.8, 33.4, 33.3, 30.4, 29.4, 26.3, 26.1, 26.0, 25.5, 25.0 ppm. FTIR ($CDCl_3$): ν 2926, 2853, 1744 cm^{-1}. EIMS: *m*/*z* 359 (16), 344 (40), 190 (100), 176 (37), 160 (32), 158 (23), 145 (25). HRMS: $C_{22}H_{33}NO_3$ requires *m*/*z* 359.2460, found *m*/*z* 359.2466.

2-[1-(Methoxycarbonyl)-3,3-dimethylpentoxy]-1,1,3,3-tetramethylisoindoline (5e). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23 (m, 2H); 7.08 (m, 2H); 4.48 (dd, J = 5.6, 7.4 Hz, 1H); 3.71 (s, 3H); 1.80 (d, J = 7.5 Hz, 1H); 1.78 (d, J = 5.5 Hz, 1H); 1.59 (s, 3H); 1.40, 1.38, 1.35 (3s, underlain by multiplet 1.35−1.26 ppm, 11H); 0.92, 0.90 (2s, 6H); 0.86 (t, J = 7.4 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 174.3, 144.8, 144.6, 127.2, 127.1, 121.4, 121.3, 81.6, 68.0, 67.7, 51.3, 42.9, 34.6, 32.0, 30.9, 29.2, 26.8, 25.6, 25.1, 8.3 ppm. FTIR ($CDCl_3$): ν 2969, 2933, 2880, 1741 cm^{-1}. EIMS: *m*/*z* 347 (10), 332 (46), 190 (100), 176 (47), 160 (29), 145 (19). HRMS: $C_{21}H_{33}NO_3$ requires *m*/*z* 347.2460. found *m*/*z* 347.2461.

2-[2-(1-Adamantyl)-1-(methoxycarbonyl)ethoxy]-1,1,3,3-tetramethylisoindoline (5f). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23 (m, 2H); 7.07 (m, 2H); 4.53 (dd, J = 8.2, 4.7 Hz, 1H); 3.72 (s, 3H); 1.95 (m, 3H); 1.49−1.76 (m, 14H); 1.41, 1.39 (2s, 6H); 1.34 (s, 3H); 1.26 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 174.3, 144.8, 144.5, 127.2, 127.1, 121.4, 121.3, 80.6, 68.0, 67.7, 51.3, 46.3, 42.3, 36.7, 31.5, 30.9, 29.1, 28.5, 25.6, 25.1 ppm. FTIR ($CDCl_3$): ν 2973, 2905, 2849, 1739 cm^{-1}. EIMS: *m*/*z* 411 (13), 396 (28), 190 (100), 175(23), 160 (21), 135 (28). HRMS: $C_{26}H_{37}NO_3$ requires *m*/*z* 411.2773, found *m*/*z* 411.2774.

2-[4,4-Dimethyl-1-(methoxycarbonyl)pent-1-oxy]-1,1,3,3-tetramethylisoindoline (5g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.22 (m, 2H); 7.08 (m, 2H); 4.59 (dd, J = 5.2, 7.2 Hz, 1H); 3.77 (s, 3H); 3.71 (dd, J = 7.2, 9.4 Hz, 1H); 3.60 (dd, J = 5.2, 9.4 Hz, 1H); 1.57 (s, 3H); 1.42 (s, 6H); 1.39 (s, 3H); 1.21 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 172.53, 144.8, 127.1, 121.5, 121.3, 85.8, 73.4, 68.2, 67.5, 61.9, 51.5, 29.7, 29.5, 27.3, 25.1, 25.0 ppm. FTIR ($CDCl_3$): ν 2977, 2933, 2874, 1744 cm^{-1}. EIMS: *m*/*z* 349 (5), 348 (4), 335 (39), 334 (90), 191 (47), 190 (93), 176 (96), 160 (100), 145 (47), 144 (43). HRMS: $C_{20}H_{31}NO_4$ requires *m*/*z* 349.2253, found *m*/*z* 349.2240; $C_{20}H_{30}NO_4$ $(M - 1)^+$ requires *m*/*z* 348.2175, found *m*/*z* 348.2173.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of isolated alkoxylamines. This material is available free of charge via the Internet at http://pubs.acs.org.

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